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Isomerization and Autoxidation of Resin Acids

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Abstract—Levopimaric acid (I), palustric acid (II), neoabietic acid (III), and abietic acid (IV) isomerized in chloroform and rapidly approached to an equilibrium state under nitrogen atmosphere in the dark (92% abietic acid (IV), 5% palustric acid (II), 3% neoabietic acid (III), but the resin acids dissolved in α -pinene or octyl alcohol did not isomerize in the absence of air. Abietic acid (IV) gave dehydroabietic acid (V) and some complex oxidation products when kept in chloroform in the presence of air. The resin acids as well as α -pinene used as solvent were oxidized in the dark, but not oxidized in octyl alcohol even in the presence of air oxygen. Homoannular dienes, such as palustric acid (II) and levopimaric acid (I), yielded dehydroabietic acid (V) on oxidation, but heteroannular dienes, such as abietic acid (IV) and neoabietic acid (III), yielded only oxygen adducts, but not dehydroabietic acid (V). Levopimaric acid (I) was presumed to be the precursor in the biosynthesis of palustric acid (II), neoabietic acid (III), abietic acid (IV) and dehydroabietic acid (V).

Introduction

It has been known that resin acids isomerized in the presence of strong acids^{1,2)} or with heat³⁾ and readily absorb air-oxygen, especially in the powder form⁴⁾.

It has been previously observed in our laboratory that resin acids in the chloroform solution are oxidized or isomerized easily to some complex compounds even when they are kept at room temperature in the dark. Subsequently we have studied on the mechanism and the reaction products in autoxidation of resin acids having conjugated double bonds. The reaction proceeded easily without using a sensitizer under day-light and the main products were dehydroabietic acid (V) and transannular peroxide^{5~7)}.

The purpose of the present work is to investigate the isomerization and oxidation products of resin acids in the solutions of chloroform, α -pinene, and of octyl alcohol when the reaction proceeds in the dark under air-oxygen atmosphere.

Experimental

Optical rotations were measured by using a JASCO DIP-SL polarimeter. NMR spectra were measured by using a Hitachi R-22 spectrometer (90 MHz) in CDCl_3 and TMS as the internal standard. Mass spectrography was conducted by using a SHIMAZU-LKB 9,000 gas chromatograph-mass spectrometer.

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Preparation of starting substances

Palustric acid was prepared from pine gum by the method of Joye *et al.*⁸⁾ $[\alpha]_D +70^\circ$; m.p. $162\sim 166^\circ\text{C}$; $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 265 (8600). Neoabietic acid (III) was obtained from pine gum by amine salt technique of Loeblich *et al.*⁹⁾; $[\alpha]_D +159^\circ$; m.p. $166\sim 169^\circ\text{C}$; $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 252. Levopimaric acid (I) was isolated from fresh pine oleoresin by the amine salt method of Loeblich *et al.*¹⁰⁾; m.p. $150\sim 151^\circ\text{C}$; $[\alpha]_D -275^\circ$; $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 273 (7200). Abietic acid (IV) was prepared from commercial rosin by the amine salt method of Harris¹¹⁾; $[\alpha]_D -110^\circ$; m.p. $170\sim 173^\circ\text{C}$; $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 241 (23000). Dehydroabietic acid (V) was isolated from the commercially disproportionated rosin by the amine salt method using 2-amino-2-methyl-1-propanol; $[\alpha]_D +163^\circ$; m.p. 171°C . Methyl esters of the acids were prepared by esterification with diazomethane.

*Isomerization of resin acids**a) Changes in specific rotation during isomerization of resin acids*

Resin acid (50 mg) was dissolved in 5 ml of chloroform (spectroscopy-grade) containing 1 % ethanol, α -pinene, and octyl alcohol respectively in a polarimeter tube. The air in the tube was completely replaced by nitrogen and the tube was sealed. The tube was kept in the dark at 25°C and readings were taken occasionally.

b) Changes in NMR spectrum during isomerization of resin acids

Resin acid (100 mg) was dissolved in 10 ml chloroform containing 1 % ethanol at 25°C . The aliquots were taken out at intervals and the solvents were removed *in vacuo*. The samples were submitted to NMR measurement. The vinyl protons of abietic acid (V) appeared at 5.78 ppm (1H, s) and at 5.37 ppm (1H, broad). The vinyl protons of levopimaric acid (I) appeared at 5.53 ppm (1H, s) and at 5.13 ppm (1H, broad). Only one vinyl proton in palustric acid (II) appeared at 5.38 ppm (1H, s). That of neoabietic acid (III) appeared at 6.20 ppm (1H, s). For quantitative determination of the component acids present in the resin acid, the respective areas of the vinyl proton signals were used throughout of this experiment. Ten milligram resin acid was dissolved in deuterated chloroform (0.5 ml) in a NMR tube. After the air was completely replaced by nitrogen, the tube was sealed and kept in the dark at 25°C and then the NMR spectra of the solution were measured at intervals.

*Autoxidation of resin acids**a) GC-Mass spectra measurement*

Methyl ester of resin acid (20 mg) was dissolved in 20 ml of chloroform containing 1 % ethanol, α -pinene, and octyl alcohol respectively and kept in the dark with occasional aeration. The aliquots were uptaken occasionally for GC-Mass

spectra measurement (5 % SE 52 on Chromosorb W at 25°C; 5 % Versamide-900 on Chromosorb W at 250°C). Peak assignment was verified by use of purified resin acids specimens. The area of a signal was compared with that of a standard specimen for quantitative purpose.

b) Preparative layer chromatography

Resin acid was dissolved in one liter of the solvents (α -pinene, spectroscopy-grade chloroform containing 1 % ethanol, and octyl alcohol) and kept in the dark with occasional aeration. The aliquots were taken at intervals and the solvent was removed *in vacuo*. The residue was esterified with freshly prepared diazomethane and was submitted to preparative layer chromatography on Merk silicagel PF-254 by using cyclohexane-ether (3 : 2) as solvent and on silica gel containing 5 % AgNO_3 by using cyclohexane-ether (20 : 1). The products were isolated with ether from the corresponding silica gel layer.

The composition of resin acids of raw oleoresin

Raw oleoresin was collected from Japanese black pine (Kuromatsu, *Pinus Thunbergii*) by inserting a glass tube with a receiver through the bark. The fresh oleoresin was immediately subjected to preparative layer chromatography to obtain the fraction containing pure resin acid (Merk silica gel PF-254, cyclohexane-ether, (20 : 1)). The resin acid mixture was analyzed by MNR. Dehydroabietic acid (V) and neoabietic acid (III) were able to be determined without being disturbed by the presence of other resin acids. Abietic acid (IV), levopimaric acid (I) and palustric acid (II) were roughly estimated although a small amount of pimaric acid was present as a contaminant. While this method can afford only approximate estimation, the error due to isomerization is believed to be low.

Results and Discussion

From the changes in specific rotation and of NMR spectra it turned out that levopimaric acid (I), neoabietic acid (III), and palustric acid (II) begin to isomerize after a certain time (I 6 hours, II 80 hours, and III 7 hours) and rapidly approach to an equilibrium state when these resin acids were dissolved together in chloroform and allowed to stand in the dark under nitrogen atmosphere (Fig. 1, 2, 3, and 4). It was found by means of NMR and GC-mass techniques that the equilibrium mixture of the resin acids consists of 92% abietic acid (IV), 5% palustric acid (II), and 3% neoabietic acid (III) (Fig. 1,5). These conjugated dienoid resin acids showed the phenomena similar to those described above even in chloroform-D (CDCl_3), as in spectroscopy-grade chloroform. When dissolved in chloroform containing a very small quantity of hydrochloric acid (about 7 ppm), these resin acids

immediately began to isomerized. By stopping the isomerization at adequate intervals and analyzing the products with GC-Mass and NMR, either levopimaric acid (I) or neoabietic acid (III) in chloroform was found to isomerize to abietic acid (IV) through palustric acid (II). But it failed to confirm the isomerization of neoabietic acid (III) to palustric acid (II) through levopimaric acid (I). Since the velocity of isomerization of levopimaric acid (I) to palustric acid (II) was very rapid than that of neoabietic acid (III) to levopimaric acid (I), the presence of levopimaric acid (I) as an intermediate was impossible to identify by means of NMR or GC-Mass although a part of neoabietic acid (III) is suspected to be isomerized to palustric acid (II) through levopimaric acid (I).

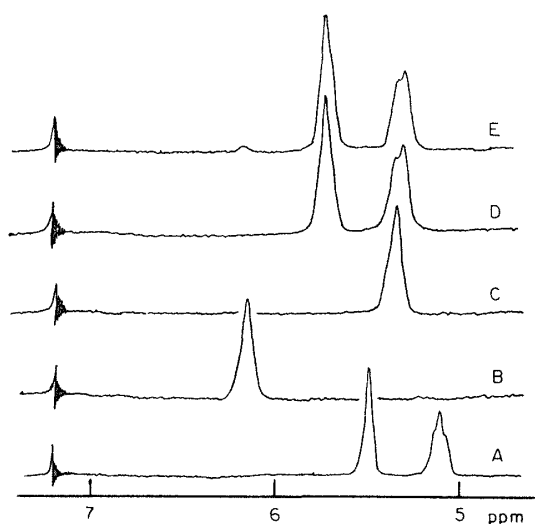


Fig. 1. NMR spectra : A, levopimaric acid ; B, neoabietic acid; C, palustric acid ; D, abietic acid; E, levopimaric acid isomerized and approached an equilibrium in CHCl_3 . Also neoabietic acid, palustric acid and abietic acid approached an equilibrium state and gave the same spectra as E.

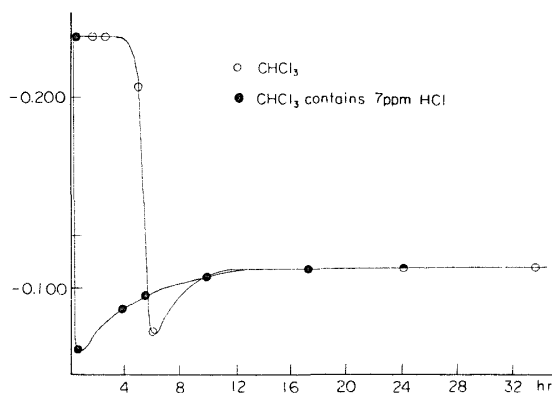


Fig. 2. Changes in rotations during the isomerization of levopimaric acid ($0.33 \times 10^{-4} \text{ M}$) in CHCl_3 .

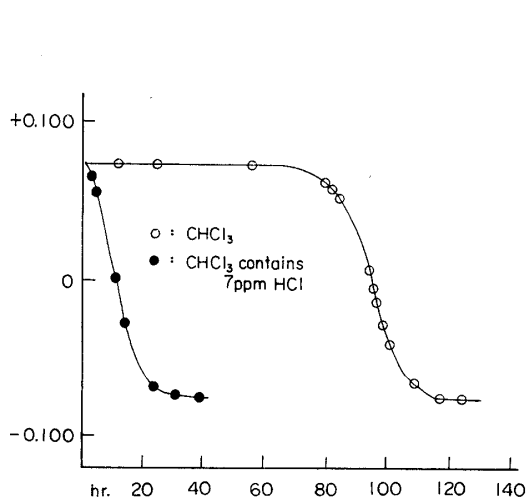


Fig. 3. Changes in rotations during the isomerization of palustric acid ($0.33 \times 10^{-4} \text{M}$) in CHCl_3 .

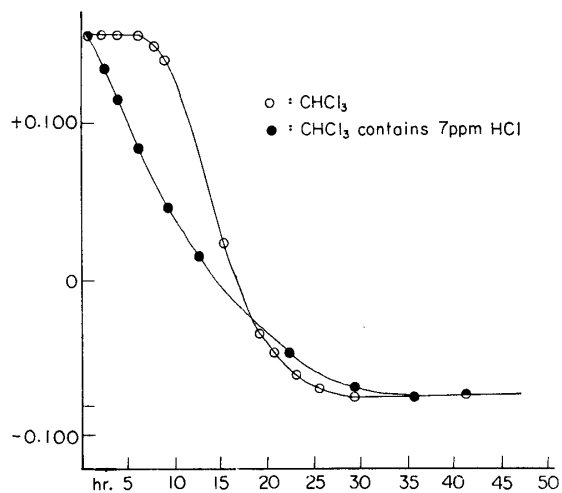


Fig. 4. Changes in rotations during the isomerization of neoabietic acid ($0.33 \times 10^{-4} \text{M}$) in CHCl_3 .

Methyl esters of these conjugated dienoid acids in chloroform also isomerized and approached to an equilibrium state.

The methyl ester of abietic acid (IV) yielded the methyl ester of dehydroabietic acid (V) (30 %) and unknown oxidation products when kept in chloroform at

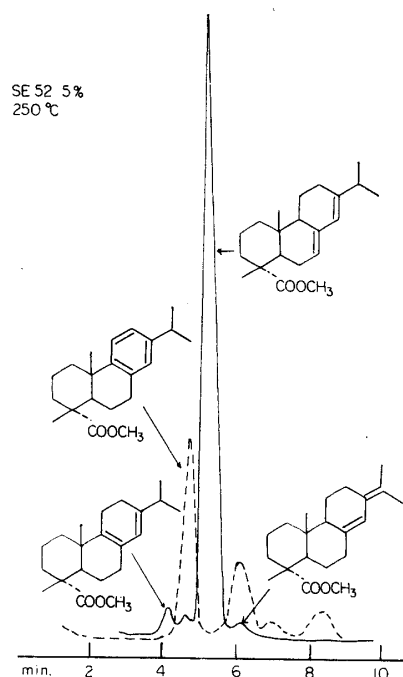


Fig. 5. Gas-liquid chromatogram: solid curve, methyl abietate kept in CHCl_3 containing 1 % EtOH for ten days in the dark under nitrogen; dotted curve, methyl abietate kept in chloroform containing 1 % EtOH for ten days under the air in the roomlight.

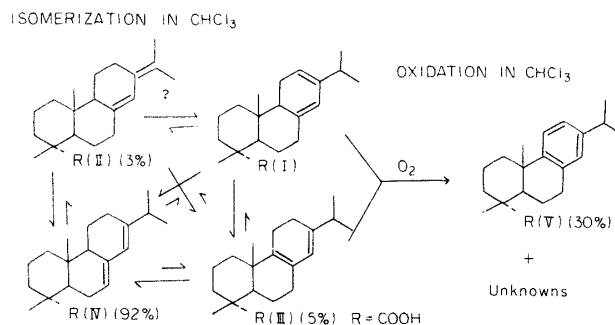


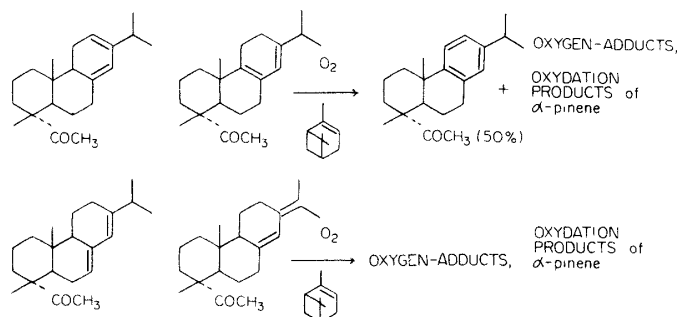
Fig. 6

room temperature for ten days under room-light and air-oxygen (Fig. 5, 6).

The methyl ester (IV), on the other hand, showed little changes even after the time when kept in chloroform for ten days under nitrogen in the dark (Fig. 5).

The resin acids (I), (II), (III), and (IV) also showed little changes when kept in octyl alcohol under nitrogen for ten days at room temperature in the dark. These resin acids showed neither isomerization nor oxidation when kept in octyl alcohol for ten days in the dark and in contact with air.

The resin acids (I), (II), (III), and (IV) and their methyl esters in α -pinene showed little changes when kept at room temperature for ten days in the dark under nitrogen. NMR and GC-Mass spectra of α -pinene in above condition also showed little changes. Those acids were, however, suffered to oxidation with aeration in the dark (Fig. 7). Methyl palustrate gave methyl dehydroabietate in about 50 % yield and the products absorbed oxygens when kept in α -pinene with aeration in the dark (Fig. 8). In the course of aeration, it was observed that α -pinene gradually absorbs oxygen and becomes more than 150 of molecular weight (MW of α -pinene 136) in company with the oxidation of methyl palustrate (Fig. 8). The oxidation products of α -pinene may be the same one with the products obtained by Moore in the autoxidation of α -pinene as is shown in Fig. 9¹²⁾. Similarly methyl dehydroabietate (50 % yield) and unknown oxidation products were obtained from levopimarate in α -pinene solution by aeration in the dark at

Fig. 7. Autoxidation of resin acids in α -pinene.

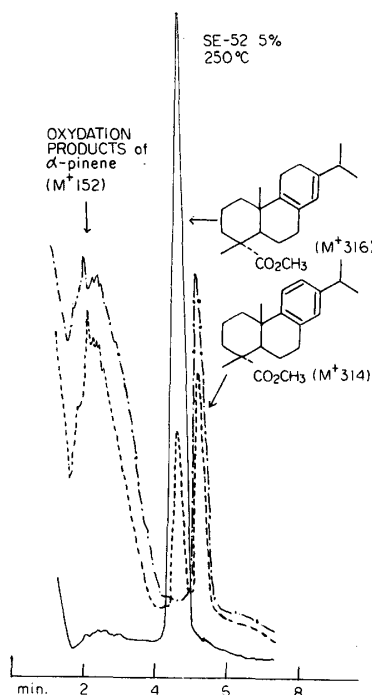


Fig. 8. GC-Mass chromatogram: —, methyl palustrate kept in α -pinene in the dark with aeration for zero day; ---, kept for 8 days; - · -, kept for 14 days.

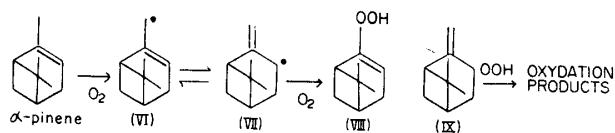


Fig. 9. Autoxidation of α -pinene in the dark¹²⁾.

25°C. Methyl abietate and methyl neoabietate in α -pinene also absorbed oxygen on aeration in the dark gave a mixture of complex oxidation products, but no methyl dehydroabietate (Fig. 7).

Methyl dihydroabietate (MW 318) was not detected by GC-Mass spectra of the resin acids oxidized with air-oxygen in the presence of α -pinene or chloroform. Both the transannular peroxides of the resin acids and other products which are formed through the peroxides^{5~7)} were not detected by TLC or NMR spectra of the oxidation products.

It is thought that the degradation products liberated by the interaction between resin acids and chloroform catalyze the isomerization of conjugated dienoid resin acids from the following facts. (a) The appearance of the isomerization products of resin acids needed a certain lag time but a very small quantity of acid caused immediately isomerization. (b) When the solution of chloroform (10ml) containing abietic acid (IV) (200mg) was kept for ten days in contact with air at 25°C and then

the solution was shaken with distilled water (2 mg), the PH of the water layer was about 3. But when only chloroform was exposed under the same condition, the PH of the aqueous layer was about 7.

Following observations indicate that dehydroabietic acid (V) is yielded by hydrogen abstraction from homoannular dienolic resin acid like palustric acid (II) or levopimaric acid (I) on the autoxidation in chloroform. (a) The conjugated dienolic acids did not isomerize each other in α -pinene in the presence of air-oxygen. (b) Heteroannular diene like abietic acid (IV) or neoabietic acid (III) gave oxidation products which absorbed oxygen, but did not yield dehydroabietic acid (V) (Fig. 7). (c) In chloroform, either heteroannular diene or homoannular diene isomerized and reached the same equilibrium state, and methyl abietate, heteroannular diene, yielded methyl dehydroabietate as one of the oxidation products in the presence of air.

Following facts mean that, in the oxidation of the resin acids in α -pinene, α -pinene is initially oxidized, and then the resulted oxidation products of α -pinene oxidize the resin acids. When the resin acids were kept in octyl alcohol in the dark in the presence or absence of oxygen, both the solvent and the solute showed little changes. When the resin acids were kept in α -pinene in the absence of oxygen in the dark, both the solvent and the solute showed little changes. But the resin acids were oxidized in company with α -pinene when the acids were kept in α -pinene in the presence of oxygen.

The following observations indicate that levopimaric acid (I) is the precursor of palustric acid (II), neoabietic acid (III), abietic acid (IV) and dehydroabietic acid (V) in Japanese black pine (*Kuromatsu*, *pinus thunbergii*) (Fig. 10). (a) Table 1, 2, Fig. 1 and 4 show that levopimaric acid (I) readily isomerizes to the double bond isomers with heat or acid. (b) Levopimaric acid (I) is the major component of resin acids in the raw oleoresin (Table 1, 2). (c) The raw oleoresin contains the great amounts of α -pinene. (d) Levopimaric acid (I) is readily oxidized to dehydroabietic acid (V) in α -pinene in the presence of oxygen. (e) The equilibrium mixture of the resin acids consists of a great deal of abietic acid (IV), small amounts of palustric acid (II) and neoabietic acid (III).

Although methyl dehydroabietate (MW 314) was yielded, it is believed that disproportionation of the resin acids did not occur because methyl dihydroabietate

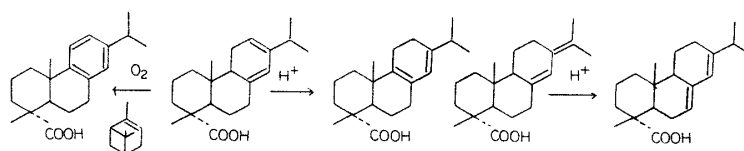


Fig. 10

Table 1. Composition of rosin products⁴⁾.

	Levopimaric acid %	Neoabietic+ palustric+ abietic acid %	Dehydroabietic+ hydroabietic acid %	Pimaric+ isopimaric acid %
Fresh oleoresin	30~50	30~50	trace	16~30
Gum rosin	0~15	65~85	trace	15~30
Wood rosin	less than 1	about 50	15~25	16
Tall oil rosin	less than 1	about 40~50	20~30	16~30

Table 2. Composition of resin acids of raw oleresin.

Levopimaric acid %	Neoabietic acid %	Dehydroabietic acid %	Abietic acid %	Palustric acid %	Pimaric acid %
50	8	8	11	16	7

(MW 318) was unable to detect.

In the present conditions, the reaction of resin acids with singlet oxygen to give transannular peroxide is very unlikely because any of the peroxide, the corresponding diepoxide, hydroxy-ketone and epoxyketone were not detected. Therefore, the oxidation reaction of the resin acids would be proceed by only a radical chain mechanism caused by radicals of α -pinene.

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